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Robust supramolecular nanocylinders of naphthalene diimide in water†

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Naphthalene-diimide (NDI)-containing nanocylinders were formed by supramolecular self-assembly in water through cooperative hydrogen bonds between bis(urea) units, reinforced by hydrophobic and aromatic-stacking interactions. The nanocylinders, decorated with poly(ethylene oxide) arms ensuring their solubility in water, exhibit a huge aspect ratio (diameter 13 nm, length 300 nm) and are extremely stable.

Inorganic 1D nanostructures have been the subject of intense interest given their specific mechanical and optoelectronic properties.[1] For their part, organic 1D nanostructures (rods, wires, filaments, tubes) can be reached through self-assembly processes and have found very diverse applications (*e.g.* optoelectronics,[2–4] biomedicine[5]) or functions (*e.g.* gelators,[6] emulsion stabilizers[7]). A decisive asset of organic self-assembled systems relies on the possibility to incorporate a specific function thanks to a precise design of the constituting building block. Of peculiar interest is the case of naphthalene diimide (NDI)-based 1D nanostructures.[8,9] This unit, in addition to be synthetically highly versatile, displays geometrical and electronic properties suitable for preparing materials ranging from biomedical to electronic applications.[10,11] Nevertheless, little attention has been dedicated to the supramolecular self-assembly of NDI-based polymers in aqueous medium. In rare examples, molecular amphiphilic NDI-derivatives have been shown to self-assemble in water into 1D nanostructures by combining the interactions inherent to the NDI core with either hydrophobic[12,13] or electrostatic[13,14] interactions. Alternatively, hydrogen bonding units such as amide,[15–17] hydrazine[18–21] or peptidic units[22–26] have been used. However, in spite of the directionality promoted by hydrogen bonds, the latter systems often self-assemble into micellar or vesicular structures[19,21] rather than into isolated rods or tubes.[16,17,22,26–28] The formation of supramolecular nanocylinders is even more difficult when the self-assembling units are decorated with polymeric arms because of the entropic penalty related to their stretching within the nanostructure.[29–32] Important achievements in this direction were recently described with amphiphilic systems featuring a NDI unit connected to a short anionic or neutral hydrophilic polymer arm through an amide hydrogen bonding unit.[16,17] Such design allows forming dynamic self-assembled vesicles that evolve within a few hours to an equilibrated cylindrical state.

Bis(urea)s are well-established self-assembling units promoting highly robust, directional and cooperative hydrogen bonds, and affording one-dimensional supramolecular structures in organic solvents[29,33,34] as well as in water.[35–42] In this communication, we demonstrate that a NDI-polymer (**PEO-NDI-U$_2$**), featuring a suitably designed bis(urea) unit, is able to self-assemble instantaneously into nanocylinders in water, and that the latter exhibit an unprecedented stability with respect to ageing, temperature or hydrogen bond competitors.

PEO-NDI-U$_2$ consists of one NDI unit functionalized by a poly(ethylene oxide) (PEO, M_n = 2000 g mol^{-1}, $Đ$ = 1.1) arm promoting water solubility, and by a bis(urea) unit (U$_2$) generating cooperative hydrogen bonds (Scheme 1). The PEO and bis(urea) parts are separated by the NDI unit on purpose, in order to favor intermolecular hydrogen bonding over intramolecular interactions between both fragments. **PEO-NDI-U$_2$** was synthesized according to a multi-step convergent approach which proved efficient (overall yield = 20% from naphthalene dianhydride) and can be in principle applied to other classes of polymers (Scheme S2, ESI†).

PEO-NDI-U$_2$ spontaneously dissolves upon dispersion in water. Remarkably, cryoTEM experiments (Fig. 1) revealed the formation of long and rigid anisotropic nanorods exhibiting a monodisperse diameter of ≈10 nm and a polydisperse length of several hundreds of nanometers. This is rather striking in

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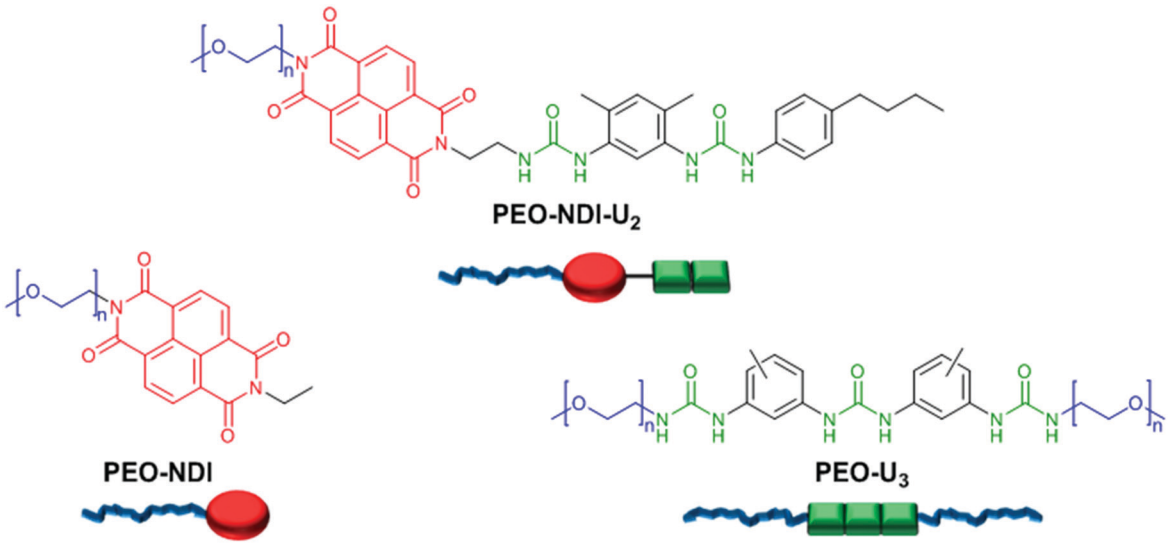

Scheme 1 Structure of **PEO-NDI-U$_2$** and model compounds **PEO-NDI** and **PEO-U$_3$**.

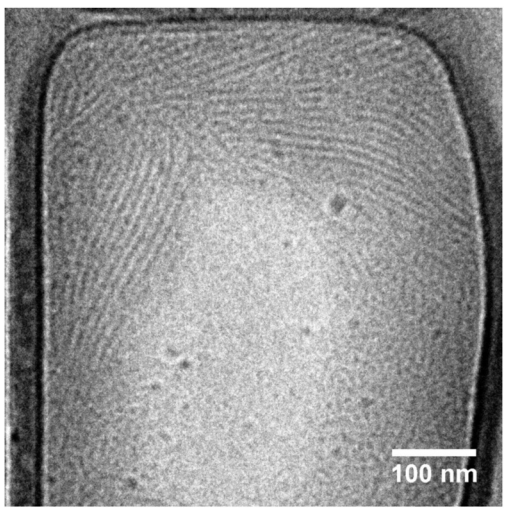

Fig. 1 CryoTEM of **PEO-NDI-U$_2$** in pure water after direct dispersion at C = 1.3 g L^{-1}.

regard to the abundant examples of the literature, which suggest that the formation of 1D structures requires additional experimental inputs such as heating (*e.g.* organo- or hydrogelators)[43,44] or addition of a cosolvent.[42] Therefore, contrary to previous observations made for NDI-based polymers involving amide hydrogen bonding functions and for which vesicles and cylinders states are successively observed,[16,17] nanocylinders of **PEO-NDI-U$_2$** are directly obtained upon dissolution in water. Such spontaneous formation of a stable cylindrical shape is ascribed to the strong hydrogen bonds between bis(urea)s that drive the supramolecular assembly (see below). Moreover, a key feature of these self-assembled nanocylinders relies on their remarkable robustness, as illustrated by a set of complementary experiments: (1) no morphological change of these 1D nanostructures was observed over several months or temperature increase (see ESI,† part 2.4.2); (2) adding 10 equivalents of $H_2PO_4^-$ ions or urea, both well-known hydrogen bonds competitors,[18,45] did not affect the nanocylindrical assemblies of **PEO-NDI-U$_2$** (see ESI,† part 2.4.5); (3) dissolving first **PEO-NDI-U$_2$** in DMSO (a solvent that prevents self-assembly by disfavoring both NDI:NDI interactions[46] and hydrogen bonding, see ESI,† part 2.4.3) before adding water, gave similar self-assembled structures as in pure water, contrary to what was observed for other systems (see ESI,† part 2.4.4).[42]

The nanocylinders were fully characterized by combination of small angle neutron scattering (SANS) as well as static (SLS) and dynamic (DLS) light scattering experiments in water and in water/DMSO (99/1 vol/vol). LS experiments revealed that differences of self-assembly in D_2O, H_2O or water/DMSO 99/1 vol/vol were negligible and that repulsive interactions could be neglected below 2 g L^{-1} so that the weight-average molecular weight (M_w) and dimensions of the supramolecular particles could be determined accurately (see ESI,† part 2.4.1). SANS and SLS were conducted on the same solution at 1 g L^{-1} in D_2O/DMSO-D_6 (99/1 vol), allowing the characterization of the particles over a broad q-range (Fig. 2, see ESI,† Section 2.3 for details). A q^{-1} dependency of the normalized scattered intensity was observed for scattering wave vector (q) values ranging from 2×10^{-3} to 2×10^{-2} Å^{-1}, confirming a rigid rod shape. The experimental data were thus fitted using a model of monodisperse homogeneous cylinders with a weight-average molecular weight $M_w = 10^7$ g mol^{-1} (corresponding to an aggregation number N_{agg} = 4000), a length L = 255 nm, a radius of the cylinder r = 6.5 nm, a z-average radius of gyration R_g = 75 nm and a mass per unit length of the cylinders $M_L = 3.5 \times 10^4$ g mol^{-1} nm^{-1} (see ESI,† part 2.3 for details). The value of r = 6.5 nm obtained from the SANS data was in very good agreement with the cryoTEM results. Moreover, the hydrodynamic radius R_h = 50 nm determined from the low q-range of the DLS data yielded a cylinder length L = 350 nm applying a previously described model,[47,48] which is also consistent with the cryoTEM and SLS data. R_g/R_h = 1.5 is also in agreement with the formation of anisotropic particles (rods).

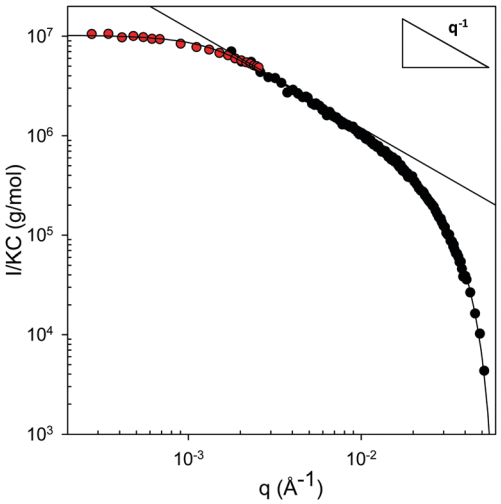

Fig. 2 Evolution of the normalized scattered intensity I/KC as a function of the scattering wave vector (q) for **PEO-NDI-U$_2$** at 1 g L^{-1} in D_2O/DMSO-D_6 (99/1 vol/vol) by combining SLS (●) and SANS (•) data. The data were fitted with a model of monodisperse cylinders (—, M_w = 10^7 g mol^{-1}, r = 6.5 nm, L = 255 nm), see details in text and ESI,† Section 2.3.1.

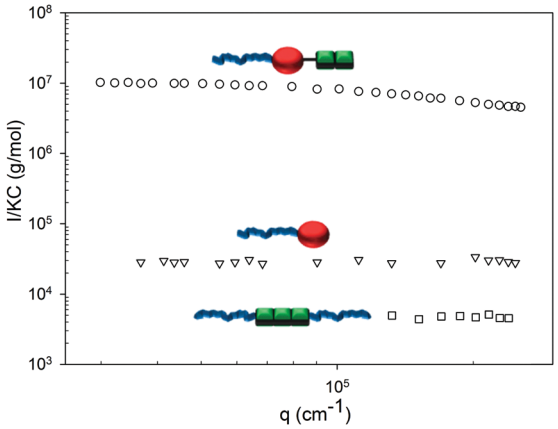

Fig. 3 Comparison of the normalized scattered light intensity I/KC as a function of the scattering wave vector (q) obtained from SLS in water for (○) **PEO-NDI-U$_2$**, at 1.9 g L^{-1}, (▽) **PEO-NDI** at 1.1 g L^{-1} and (□) **PEO-U$_3$** at 10 g L^{-1}.

In order to gain a thorough understanding of the forces driving the remarkably stable **PEO-NDI-U$_2$** self-assembly process, complementary scattering (light and neutron) experiments were led in various solvents (see ESI,† part 2.4.6). The results revealed that **PEO-NDI-U$_2$** not only self-assembles in water, but also in other polar organic solvents – no matter whether they are strong hydrogen bond competitors (methanol, known to destroy other assemblies combining NDI and hydrogen bonding units)[49,50] or not (acetonitrile) – as well as in a non-polar organic solvent (toluene). These results and the fact that NDI:NDI interactions are favored in polar solvents[46] suggest that the self-assembly in water (as well as in acetonitrile and methanol) could be driven solely by solvophobic and aromatic stacking interactions involving the NDI unit. To clarify this point, the model compound **PEO-NDI** was synthesized (Scheme 1 and see ESI,† part 1.3.1) and its self-assembly was studied in water.

PEO-NDI, which lacks only the bis(urea) unit compared to **PEO-NDI-U$_2$**, hardly aggregates in water and leads to spherical particles rather than to cylinders (Fig. 3 and Fig. S32, ESI†), definitely proving the key role of hydrogen bonding for the self-assembly into nanocylinders of **PEO-NDI-U$_2$**. **PEO-NDI-U$_2$** was also compared to the recently described **PEO-U$_3$** system,[42] devoid of any NDI moiety and featuring a tris(urea) unit directly connected to two PEO arms. The latter was shown to remain as unimers in water,[42] even though tris(urea) derivatives are known to self-associate more efficiently than bis(urea) ones.[29] Overall, these results show that: (i) hydrogen bonds provided by the bis(urea) units are of utmost importance to drive the formation of 1D supramolecular structures; (ii) the latter must be reinforced by hydrophobic/aromatic-stacking interactions provided by the NDI unit[51] to promote the formation of long supramolecular nanocylinders in aqueous medium; (iii) the combination of both types of interactions is so strong that the nanocylinders formed by **PEO-NDI-U$_2$** are resilient towards temperature, time or addition of hydrogen bond competitors.

Considering that bis(urea)s self-assemble through hydrogen bonding along the cylinders axis and are separated by an intermolecular distance of 0.46 nm within the self-assembly,[52,53] the M_L value determined by SLS and SANS suggests that the cross-section of the cylinders consists of ≈6 molecules (see ESI,† part 2.3.2.c for details). On this basis, we propose a possible self-assembling model of **PEO-NDI-U$_2$** in water (Fig. 4), which accounts for the observed cylindrical organization. We note that the size of **PEO-NDI-U$_2$** ranges between 5 and 19 nm depending on the degree of stretching of the PEO arm (see ESI,† part 2.5). The proposed model is therefore compatible with the radius of the cylinders determined by SANS. Moreover, this model would also account for the critical role of NDI units, which shield the directional hydrogen bonds between bis(urea)s from the competing role of water or PEO arms.

In conclusion, the design of an NDI derivative featuring a hydrophilic PEO substituent and a bis(urea) hydrogen bonding moiety has allowed an unprecedented direct access to highly stable organic self-assembled nanocylinders in water. Those long structures (*ca.* 300 nm) have been thoroughly characterized by a

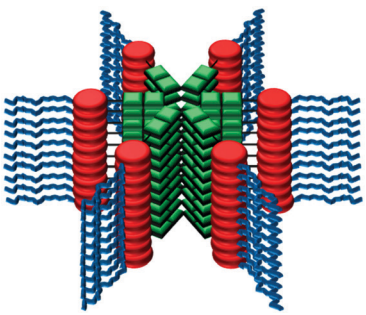

Fig. 4 Possible model for the self-assembly of **PEO-NDI-U$_2$** in water into supramolecular cylinders *via* hydrogen bonds reinforced by hydrophobic interactions.

full set of different techniques. These studies confirm the key roles of each counterpart (*i.e.* cooperative hydrogen bonding between bis(urea) units, hydrophobic and aromatic-stacking between the NDI moieties) and the need to combine them in a synergistic and well-balanced way to afford the target 1D nanostructures. This result opens wide perspectives towards the preparation of self-assembled π-functionalized 1D-nanocylinders from polymer-based units, an approach that we currently develop.

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Conflicts of interest

There are no conflicts to declare.

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